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— COMMITTED TO PROTECTION OF THE ENVIRONMENT —

DEVELOPMENT AND EVALUATION OF ANALYTICAL METHODOLOGIES USED IN RMA SOIL INVESTIGATIONS

EBASCO SERVICES INCORPORATED
R. L. Stollar and Associates
California Analytical Laboratories, Inc.
DataChem, Inc. Geraghty & Miller, Inc.

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ROCKY MOUNTAIN ARSENAL

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April 1988

Prepared by

Ebasco Services, Inc.
R.L. Stollar and Associates
California Analytical Laboratories, Inc.
DataChem, Inc., Technos, Inc., Geraghty & Miller, Inc.

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THE PURPOSE OF THIS REPORT IS TO DESCRIBE THE PHILOSOPHY AND PROTOCOLS OF THE ANALYTICAL CHEMISTRY PROGRAM SUPPORTING THE RMA REMEDIAL INVESTIGATION. THE PHASE I ANALYTICAL METHODOLOGIES AND ANALYTICAL REPORTING LIMITS AND THOSE SCHEDULED TO BE EMPLOYED UNDER PHASE II OF THE RMA SOIL INVESTIGATIONS ARE REVIEWED. THE POSSIBILITY AND DESIRABILITY OF LOWERING THESE LIMITS ARE ALSO CONSIDERED.

SECTIONS OF THE REPORT DETAIL INFORMATION ON:

1. PROGRAM CONSTRAINTS
2. OPERATIONAL PROCEDURES
3. PROGRAM EVALUATION.

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DEVELOPMENT AND EVALUATION OF
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1.0 INTRODUCTION

1.1 Objective

The purpose of this paper is to describe the philosophy and protocols of the analytical chemistry program supporting the Rocky Mountain Arsenal (RMA) remedial investigation (RI). The Phase I analytical methodologies and analytical reporting limits, and those scheduled to be employed under Phase II of the RMA soil investigations are reviewed. The possibility and desirability of lowering these limits are also considered.

The RI poses special problems which are associated with the vast area requiring investigation, the diversity of sample types, the unique analytes, the range of contaminant chemical concentrations, and the schedule for completing the program. Analytical factors such as method specificity, sensitivity, speed, ability to accommodate wide ranges of concentration, and quality control requirements have been balanced to provide the USATHAMA-certified methods used in the RI.

Several of the methods for organic analytes have been improved in sensitivity between Phases I and II. The organic compounds are determined using gas chromatography/mass

spectrometry (GC/MS) under Phase I and gas chromatography under Phase II. These improvements are documented and discussed.

Phase I inorganic methods have continued into Phase II with relatively little modification. Analytical methods now in use include inductively coupled plasma (ICP) and atomic absorption (AA) spectrometry. These are the most appropriate for the chosen suite of metals. Inorganic anions are determined by ion chromatography (IC).

The following discussion describes the analytical program with focus on its strategy, and quality assurance and quality control (QA/QC) requirements for the organic (volatiles and semivolatiles) and the pesticide analytes. The interaction between RI requirements, program constraints, and analytical program accommodation will become apparent.

1.2 Program Strategy

Due to the magnitude, diversity, and unknown nature of potentially contaminated soil at RMA, a two-phased investigative approach was developed between September 1984 and March 1985 under the direction of the Program Manager-Rocky Mountain Arsenal Contamination Cleanup (PM-RMACC). The program was developed to quickly identify sources of contamina-

tion and expedite cleanup to prevent the further migration of contaminants.

The Phase I soils investigations began in early 1985. The purpose of the Phase I program was to screen for potential chemical contaminants and physical threats (i.e., potential unexploded ordnance (UXO) or buried metal containers) throughout RMA in the unsaturated soils. Based upon the Phase I results, Phase II programs were developed on a site-by-site basis to collect additional data necessary to quantitatively assess the boundaries and depths of suspected areas of contamination.

Most aspects of the RMA RI are generally consistent with the RI process required under CERCLA (Comprehensive Environmental Response Compensation Liability Act), SARA (Superfund Amendments Reauthorization Act), and the NCP (National Contingency Plan) and as specified in Guidance on Remedial Investigations under CERCLA, June 1985.

The major requirements of a typical CERCLA investigation are as follows: (a) the identification of waste generators, their operations, and compounds handled; (b) the identification of potential contamination and migration pathways; (c) literature review of the environmental mobility and fate of characteristic (target) compounds; (d) the de-

velopment or identification of existing analytical methodologies; (e) the collection of samples; and (f) data analysis. A more detailed description of these topics as they relate to the RMA RI program follows.

Historical data were reviewed to locate reports and operational records pertaining to the handling of chemical products on the post. Both the Army and lessees (Julius Hyman and Company, Colorado Fuel and Iron, and Shell Chemical Company) manufactured chemicals and handled products that were shipped to RMA. The lessees predominantly produced pesticides, but a caustic chlorine production plant was also operated. The Army manufactured and demilitarized chemical agent materials including Levinstein mustard, lewisite, and incendiary devices. These operations were carried out in the South Plants area manufacturing complex. GB nerve agent (Sarin) manufacturing and demilitarization were carried out by the Army in the North Plants area.

From the data review, listings of compounds characteristic of Army and lessee operations at RMA were generated. A smaller listing (target list) of compounds was developed from this comprehensive list. In total, 49 compounds were identified on the initial target list (42 organics and 7 metals). This target list, Table 1.2-1, provided the basis for the initial selection of the RMA RI program analytes.

Table 1.2-1. Initial List of RMA Target Compounds

Volatile Organics

- Benzene
- Bicycloheptadiene
- Carbon tetrachloride
- Chlorobenzene
- Chloroform
- 1,1-Dichloroethane
- 1,2-Dichloroethane
- trans-1,2-Dichloroethylene
- Dimethyldisulfide
- Ethylbenzene
- m-Xylene
- Methylene chloride
- Methylisobutyl ketone
- Tetrachloroethylene
- 1,1,1-Trichloroethane
- 1,1,2-Trichloroethane
- Toluene
- Trichloroethylene
- o- and/or p-Xylenes

Semi-Volatile Organics

- Aldrin
- Atrazine
- Chlordane
- Chlorophenylmethyl sulfide
- Chlorophenylmethyl sulfone
- Chlorophenylmethyl sulfoxide
- Dibromochloropropane
- Dicyclopentadiene
- Dieldrin
- Diisopropylmethylphosphonate
- Dimethylmethylphosphonate
- Dithiane
- Endrin
- Hexachlorocyclopentadiene
- Isodrin
- Malathion
- 1,4-Oxathiane
- p,p'-DDE
- p,p'-DDT
- Parathion
- Supona
- Vapona

Table 1.2-1. Initial List of RMA Target Compounds

Inorganics
Arsenic
Cadmium
Chromium
Copper
Lead
Mercury
Zinc

The migration pathways of concern at RMA are soil, ground and surface water, air, and biota. These media are the same as those required to be addressed under a normal CERCLA investigation. This paper addresses only the soil study and related analytical methodologies. However, the remaining media have been and currently are being investigated.

Environmental mobility and fate of the target compounds, as well as others related to RMA activities, have been investigated. These target compounds include probable daughter products of key RMA contaminants. Interactions between ground-water and soil contaminants are being considered as part of later phases of the RI program.

The analytical methodologies chosen for the RMA target compounds were based largely on existing United States Environmental Protection Agency (USEPA) procedures. For a few compounds, methods were developed since none previously existed. In all cases, the analyses were certified by USATHAMA (U.S. Army Toxic and Hazardous Materials Agency). The methods were standardized as much as possible considering the differences in instrumentation among the participating laboratories. This standardization maximized the likelihood that all laboratories in the RMA program would generate acceptable data of comparable quality (see Section 3.2 of this report).

The methods chosen provided positive identification and semiquantitative results for the target organic and pesticide analytes under Phase I. The methods selected for the metals and inorganics are quantitative under Phases I and II. This level of quantitation exceeds the requirement of qualitative determination, as specified under CERCLA. Since it was apparent from earlier studies that many of the target analytes were present in some portions of the site, the need was for early definition of the spatial distribution of these analytes. Semiquantitative procedures offered the opportunity to obtain approximate concentration gradients. This information would improve the efficiency of Phase II studies by outlining the areas requiring further sampling. In view of the extensive area involved, early definition of the most seriously contaminated areas was essential. Since qualitative analysis would not distinguish barely detectable concentrations from "hot spots," such spatial resolution would be poor at best. Phase II of the RI provides quantitative data (a more detailed discussion of the analytical procedures is given in Section 3.2 of this report).

Soil, biota, air, and water samples are collected according to specified protocols. Details are available in the specific technical plans. This improves consistency between measurements and minimizes the amount of data variability attributable to sampling practices.

Data analysis is the link between the RI program and the feasibility study (FS). Interpretation of the data helps in the evaluation of the necessary remediation, as well as in the selection of appropriate cleanup options. This aspect of the RMA RI/FS program is just beginning.

Although the above discussion is brief, it does demonstrate that the RMA RI/FS program is consistent with a normal CERCLA investigation. The RMA program design is consistent with the RI guidance document prepared by the USEPA and has been revised to be in accordance with SARA and NCP requirements, thus demonstrating that it has been developed, revised, and updated with regard to federal regulations at all times.

2.0 PROGRAM CONSTRAINTS

The five major forces in the selection of the remedial investigation, Phases I and II, analytical methodologies and reporting limits were

1. Limitations of sampling.
2. Laboratory capabilities.
3. Schedule of remedial investigation.
4. Health and safety requirements.
5. Cost effectiveness.

Technical plans for the original soil investigations were prepared in the fall of 1984. At that time, the program milestones were:

January 1987 - Completion of Phase I Programs

July 1987 - Completion of Phase II Programs

The original task effort at RMA included the investigations of Section 36 sites (including Basin A) and the South Plants area. These two contracts (Tasks 1 and 2, respectively) were awarded in September 1984. Many additional tasks have been added to the investigation since 1984. These include tasks related to the soil investigation and they are listed below.

Task	Description	Contract Award Date
6	Sections 26 and 35	4/85
7	Lower Lakes	4/85
10	Sewers	9/85
11	Hydrazine Area	10/85
12	Derby Lakes Area	9/85
14	Army Sites North	9/85
15	Army Sites South	3/86
24	Building Survey and Spill Sites	9/86
42	North Plants Area	9/86

The above are contract award dates; each actual field investigation began a few months later, after preparation and approval of technical and management plans.

2.1 Limitations of Sampling

Sampling limitations consist of two types: the physical collection of the samples and also the characteristics of the sample that must be considered in its analysis. This sampling component of a field investigation is more significant when soil samples are collected than when water samples are collected because soils are much less homogeneous than water.

The protocols for sample collection are given in the technical plan for each specific task. In potentially uncontaminated areas, samples were collected in each borehole at depths of 0 to 1 feet and 4 to 5 feet. These two samples were composited to provide the most cost- and time-effective method of evaluating the soil quality. In areas of potential contamination, the sampling intervals for each borehole were 0 to 1, 4 to 5, 9 to 10, 14 to 15, 19 to 20, and 29 to 30 feet. Samples taken below 30 feet were collected at 10-foot intervals.

The collection of samples at intervals throughout the length of a borehole is common practice. However, due to the magnitude (approximately 17,000 acres) and diversity of the site, this standard protocol constrains the program. The number of samples required to spatially characterize potentially contaminated and uncontaminated areas is large.

Although the RMA RI program is not limited by the magnitude of the site, it is constrained by the maximum amount of sampling and analysis that can be performed in a short time period. The number of samples to be collected and analyzed is also affected by laboratory capabilities and by the RI schedule.

Special care was used to develop detailed procedures for sample handling in the field. Determination of volatile organic compounds required the rapid processing of cores to preclude loss due to volatilization. Ends of core sections were scraped to produce samples for agent screening (see Section 2.4). Cores were quickly capped and refrigerated and then shipped to the laboratories in refrigerated containers. The holding time for these samples is 7 days. As a result, the number of samples sent to the laboratory was regulated to ensure that all samples could be processed within the 7-day holding time.

In addition to the sampling program being carried out by the Department of the Army (as discussed above), Shell Chemical Company's consultant Morrison-Knudsen Engineering, Inc. (MKE) is splitting samples with the Army in a parallel soil-sampling program. MKE takes samples at selected borings. As the particular site technical plan is released to MKE, they have approximately 1 week to designate the locations from which they want samples. The sampling schedule

is arranged such that the MKE samples are collected concurrently. MKE takes a laboratory-prepared split of the 0 to 1 foot sample and then a subsample of the 1 to 4 foot sample, which is collected in a polybutyrate tube. As with the Army contractor, collected samples are also screened for chemical agents (see Section 2.4 of this report).

The second limitation with respect to sampling is related to the characteristics of the soil sample itself. Although appearing homogeneous to the eye, soil is a complex mixture of inorganic mineral matter of a wide range of particle sizes and organic matter in solid and dissolved forms. Natural soil contains variable amounts of metal ions that are associated with the soil particles. Thus the smaller the analytical sample, the more prone it becomes to showing variability resulting from natural heterogeneity. To minimize this contribution to analytical uncertainty, attention was given to homogenization procedures prior to subsampling. Despite intensive efforts to minimize heterogeneity, it still remains as the largest source of uncertainty in analytical results. Unfortunately, homogenization of soils with respect to volatiles is not feasible. Thus, subsamples for volatile organic compound determinations were removed prior to sample homogenization.

To determine the relative significance of soil composition data from suspected contaminant sources, ambient or

background soil quality must be established. For the RMA RI, baseline soil composition was determined for arsenic, cadmium, chromium, copper, mercury, lead, and zinc (As, Cd, Cr, Cu, Hg, Pb, and Zn). Three lines of investigation were followed to determine baseline metal concentrations. The first was a literature search to determine natural ranges of chemical elements in soils, specifically soils of the western United States. The second method utilized was the chemical analysis of a bulk soil sample (reference soil sample) that was collected and homogenized. It serves as a soils matrix for quality control (QC) measurements to be made by the project laboratories and helps to define the variability of analytical measurements in the various contractor laboratories by providing background soil composition. The final method was the tabulation and evaluation of soil-quality data from nonsource areas of RMA.

The reference soil sample was collected from an area just northeast of RMA. This area was chosen to represent the soil types at RMA and the typical background analyte concentrations in a nonsource site. This bulk sample was dried and homogenized, and served as the substrate for laboratory certification of analytical methods and as the blank used for lot-by-lot laboratory QC procedures. A sample of this reference soil is included in all analytical lots and provides an unprecedented body of data relating to soil composition and measurement variability which is useful in the

data interpretation process. However, the inclusion of the reference soil with each analytical lot imposes a necessary further constraint on the laboratory capabilities (see Section 2.2).

2.2 Laboratory Capabilities

The generation of reliable analyses for a large number of analytes in soil samples demands expeditious completion of the analyses. Many of the analytes exhibit significant losses due to volatilization, biodegradation, etc., relatively soon after sampling. Consequently, holding times must be rigorously observed both in the field and in the laboratory. Sampling teams must (a) have adequate time to clean apparatus carefully to avoid cross-contamination, (b) prepare detailed logs and follow all labeling requirements, and (c) promptly cool and ship samples to minimize analyte losses.

It was determined that a single laboratory could not perform all the required analyses while adhering to the sample holding times and RI schedule. The total number of laboratories contracted to perform the analyses was limited to six, thereby allowing extensive standardization of analytical methodology, quality assurance/quality control (QA/QC) coordination and an adequate schedule of audits. Since each laboratory has limited sample processing and

analysis capabilities, there was an upper limit to the numbers of samples they could process within established holding times.

Approximately 10,000 samples are to be collected for the RMA remedial investigation. This figure represents all Phase I and II samples collected from all media (i.e., ground and surface water, air, biota, and soil). The Phase I soil samples represent about half of this value.

From the perspective of optimizing spatial resolution of various analytes, it was necessary to take as many samples as possible. This objective was tempered by the practical constraints enumerated above. The outcome was a plan to take as many samples as possible without compromising the quality of the data generated.

2.3 Remedial Investigation Schedule

The original estimated date for completion of the RI was July 1987. This has been extended to March 1988, and currently discussions are ongoing to extend the date to December 1990. One reason for the extension of the date was the inclusion of task efforts in addition to the original Tasks 1 and 2 efforts. Although the RI schedule and the laboratory capabilities are unique constraints, they are

also related; the schedule can only be met if the samples can be collected and analyzed in a timely manner.

The schedule for the RI was discussed with and then determined by the experience of key individuals (laboratory and PM-RMACC personnel and noted technical experts). An appropriate time needed to complete the feasibility study and cleanup action was determined. The PM-RMACC is dedicated to the timely completion of the field programs so that the actual remediation of RMA can begin.

2.4 Health and Safety

Since RMA was a facility involved in the production and demilitarization of chemical agents and also the production and testing of incendiary devices, health and safety requirements for the field investigation were extensive. They included OSHA-regulated health and safety requirements, as well as special procedures to deal with Army chemical agents and the possibility of encountering unexploded ordnance (UXO) during drilling.

The health and safety aspect of sampling addresses the potential problems posed by chemical contaminants including chemical agent materials and UXO. Personnel who perform drilling and geologic logging and sampling tasks are required to be protected from vapor and direct contact with

contaminated soil. The protection includes protective clothing and breathing apparatus ranging through standard levels of protection to level B. The level is determined on a site-by-site basis by the safety officer.

The process of suiting up and decontamination requires considerable time out of the working day. Working in protective clothing and at times with respirators also cuts efficiency severely. In summer weather, working times are limited because of the heat. All of these factors combine to reduce the rate of sample acquisition. Additional field personnel were added to minimize excessive delays.

Health and safety monitoring procedures during drilling operations determine the level of protection for sampling personnel. The presence of explosive gases, organic vapors, and chemical agents in the borehole, samples, and the working (breathing) zone, requires that drill-rig operators commence drilling at level B to level C protection. If no contaminants are detected, then drilling may continue at the D level.

Geophysical techniques were employed to "clear" all proposed drilling locations where the presence of buried metal objects or UXOs was suspected. This was necessary to detect the presence of any UXO or other potentially hazardous buried objects. Magnetometer and electromagnetic

(EM) surveys were performed. These techniques "cleared" drilling locations to a depth of 5 feet. This clearing requirement limits the speed of the drilling and soil sampling program and can delay sampling from a few days to a few weeks.

High concentrations of combustible gases in the work area near a borehole will necessitate evacuation and venting or gas displacement before operations resume. Organic vapors are surveyed using a HNu-Photoionization Detector and OVA-Flame Ionization Detector (OVA - organic vapor analyzer) at the respiratory zone, in and near the borehole, and at the surface of drilling cuttings and core samples. Potential respiratory hazards can be identified using these detectors.

Tests for chemical agents are performed continually with the Army M-8 alarm. If a positive test is obtained, all operations cease and appropriate parties are notified.

No soils from agent-contaminated boreholes could be transported to off-post laboratories, even if only one sample from the borehole contained a chemical agent. Therefore, chemical agent screening analysis was also conducted for all soil samples using the M18A2 colorimetric detector tubes. Detection of chemical agents requires the analysis

of the 1-foot core sample by the RMA laboratory. Small samples are scraped from both ends of each 1-foot core section. These samples are composited over the sampling day, and chemical agent analysis is conducted using gas chromatographic methods by the RMA laboratory. It is necessary to composite the samples in order to rapidly identify agent-contaminated samples so that the overall sample-holding time is not exceeded. Discrete subsamples are also maintained to identify contaminated locations if the composite tests positive for agents.

All CERCLA investigations require site-specific health and safety plans, and the RMA program is no exception. However, health and safety requirements can be considered a program constraint for this project. The extra measures to ensure health and safety with regard to UXO and agent materials limit the pace of the sampling program.

2.5 Cost Effectiveness

Cost effectiveness was considered in the development of the RI program, but it was not an overriding consideration. In terms of analytical capabilities, cost effectiveness is directly related to time for the analysis. As the time required for preparation and analysis of samples increases, the cost per sample also will increase. The time and resulting cost cannot be indefinitely increased because of

program schedule needs. Increased time and cost per sample tend to reduce the number of samples analyzed, thereby reducing spatial resolution. Since the initiation of the RI program, the allocated budget of the program has more than quadrupled. The increased budget was used for additional tasks and items needed to perform a complete remedial investigation. Hence, cost was only a constraint in terms of equipment and manpower limitations and not as a cost ceiling set for RMA program expenditures.

3.0 OPERATIONAL PROCEDURES

This section will detail the operational concepts used in the development of the RMA RI program. These include the identification of the initial target list compounds and the program development strategy. The analytical procedures, QA/QC, and determination of the certified limits of quantitation are discussed.

The RI program was developed to identify areas of contamination of wide concentration ranges that would allow a reasonable project lifetime while also providing spatial resolution of contaminated zones on RMA. Because early delineation and cleanup of contaminated soil zones were the major objective, it became important to expedite the processing of the requisite number of samples within the project's lifetime.

3.1 Target List Compounds

As stated previously, a target list of compounds was developed to characterize RMA contamination. The chemicals selected as target analytes for the monitoring program were based on some or all of the following criteria:

- The compound is a suspected contaminant because it was produced or disposed of in large quantities at RMA;
- The compound is toxic;
- The compound is persistent in the environment;
- The compound was an Army agent material, or degradation product of an agent material, likely to still be present in the RMA environment;
- The compound is currently included in monitoring and investigatory programs being carried out on and in the vicinity of RMA.

In total, 49 analytes were identified for the initial target list (42 organics and 7 metals). These 49 analytes also formed the basis of the Phase I analytical parameters. As the field program progressed, additional analytes were identified as warranting classification as a target compound. As a result, the Phase I listing of target compounds has been supplemented and now includes 61 compounds. Also, additional parameters were added under Phase II of the RI. Since the Phase I investigation was completed for a number

of sites before the target list was supplemented, these supplemental Phase I analytes were and are being included as part of the Phase II site investigation. Table 3.1-1 lists the current Phase I and II analytes.

3.2 Analytical Procedures

As stated previously, the RI program was divided into two phases. The objective of Phase I was to locate areas of significant contamination, while that of Phase II is to more accurately define the extent of contamination. Analytical procedures were selected such that these objectives could be addressed.

An important factor in the construction of the analytical strategy was the basic requirement that a large number of analytical samples be processed in a reasonable length of time. The vast area (approximately 17,000 acres) requiring definition mandated a large number of samples in order to provide suitable spatial resolution. Because there was presumed to be a large contrast between contaminated and nonsource areas or depths, a larger volume of samples with their associated quantitation limit was preferred over the option of analyzing fewer samples with potentially lower limits of quantitation.

Table 3.1-1. Phases I and II Target Analytical Parameters of RMA Soils Remedial Investigation

Phase I[1]

Volatile Organics

- Benzene
- Bicycloheptadiene
- Carbon tetrachloride
- Chlorobenzene
- Chloroform
- Dibromochloropropane[2]
- 1,1-Dichloroethane
- 1,2-Dichloroethane
- trans-1,2-Dichloroethylene
- Dicyclopentadiene[2]
- Dimethyldisulfide
- Ethylbenzene
- Methylene chloride
- Methylisobutyl ketone
- Tetrachloroethylene
- 1,1,1-Trichloroethane
- 1,1,2-Trichloroethane
- Toluene
- Trichloroethylene
- m-Xylene
- o- and/or p-Xylenes

Semi-Volatile Organics

- Aldrin
- Atrazine
- Chlordane
- Chlorophenylmethyl sulfide
- Chlorophenylmethyl sulfone
- Chlorophenylmethyl sulfoxide
- p,p'-DDE
- p,p'-DDT
- Dibromochloropropane[2]
- Dicyclopentadiene[2]
- Dieldrin
- Diisopropylmethylphosphonate
- Dimethylmethylphosphonate
- Dithiane
- Endrin
- Hexachlorocyclopentadiene
- Isodrin
- Malathion
- 1,4-Oxathiane
- Parathion
- Supona
- Vapona

Organonitrogen Compounds

- n-Nitrosodimethylamine
- n-Nitrosodi-n-propylamine

Hydrazines

- Hydrazine
- Methylhydrazine
- Unsymmetrical dimethyl hydrazine

Agent Products

- Chloroacetic acid
- Fluoroacetic acid[2]
- Isopropyl methyl phosphonic acid
- Methyl phosphonic acid[2]
- Thiodiglycol

Metals

- Arsenic
- Cadmium
- Chromium
- Copper
- Lead
- Mercury
- Zinc

Inorganics

- Chloride
- Fluoride
- Sulfate

Table 3.1-1. Phases I and II Target Analytical Parameters of RMA Soils Remedial Investigation

Phase II[1]	
Phase I Listing and Volatile Organics	Agent Products
1,1-Dichloroethene	Diisopropylaminoethanethiol[3]
	Dimethyl arsenous acid[3]
	Methyl arsonic acid[3]
	Tributylamine[3]

[1] The soil monitoring program of the RI is performed as two phases. Phase I identifies potential contamination sources while Phase II defines the areal and vertical extent of contamination.

[2] These compounds are analyzed for under both compound classifications.

[3] Certification for this analyte has not yet been received.

The methods used in Phase I for soil analyses are modified forms of USEPA 600 and 8000 series methods. In May 1984, the techniques and desired limits of detection (LOD) were proposed. As Table 3.2-1 indicates, analyses were based upon established methods; the exception is dibromochloropropane (DBCP). The five metals (cadmium, chromium, copper, lead, and zinc) were analyzed using inductively coupled plasma (ICP) techniques.

Gas chromatographic/mass spectrometric (GC/MS) methods were chosen for the target organic analytes since they would provide positive identification and semiquantitative information on levels of soil contamination. Simultaneously, they provide data for the identification of additional compounds (nontarget analytes) that may need to be included under the Phase II program. GC/MS allows for the comparison of sample spectra, with known spectra for the target compounds and also for library-stored values. Hence, some nontarget analytes can be tentatively identified from Phase I analyses. A separate method (gas chromatography/electron capture-GC/EC) was initially used for DBCP analysis. It was later dropped from the soils program after it was determined that DBCP was amenable to inclusion in the GC/MS methods.

The ICP method was chosen for the metals analyses since it allows the determination of several metals simultaneously. Atomic absorption (AA) methods were used for arsenic

Table 3.2-1 Proposed Soil Analyses and Limits of Detection (LOD) for Phase I Analyses, May 1984.

Analyte	Method	Desired LOD
Chlorinated Pesticides		
Aldrin	3550, 8080[1]	0.1 ug/g[4]
Endrin		0.1 ug/g[4]
Dieldrin		
Dibromochloropropane	Contractor Developed	0.1 ug/g[4]
GC/MS Volatile Screen	3550, 8270[1]	10 ug/g[1]
GM/MS Volatile Unknown Ident.		
GC/MS Semi-Volatile Screen	3580, 8270[1]	10 ug/g[1]
GC/MS Semi-Volatile Unknown Ident.		
Anions	EPA 300.0[3]	
Nitrate		1 mg/g[4]
Chloride		0.1 mg/g[4]
Fluoride		1 mg/g[4]
Sulfate		1 mg/g[4]
Phosphate		1 mg/g[4]
Metals		
Chromium	3050, 7190[1]	1 ug/g[4]
Cadmium	3050, 7130[1]	1 ug/g[4]
Mercury	7471	0.2 ug/g[4]
Lead	3050, 7240[1]	1 ug/g[4]
Copper	3050	1 ug/g[4]
Arsenic	3050, 7060[1]	1 ug/g[4]
Magnesium	3050	10 ug/g[4]
Calcium	3050	10 ug/g[4]
ICP Screen (Ba, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl, Zn, Sb, As)	200.7[3], 6010[1]	5-500 ug/g[2]
Ancillary Measurements		
EP Toxicity		--
Anion Exchange Capacity		
Cation Exchange Capacity		
Percent Soil Fines	ASTM	

[1] SW-846 2nd Ed.
[2] Assumed for purpose of bid.
[3] EPA 600/4-84-017 Mar 1983 "The Determination of Inorganic Anions in Water by IC."
[4] By comparison with water.

ug/g - micrograms per gram
mg/g - milligrams per gram

(graphite furnace) and mercury (cold vapor) due to the inability of ICP to quantitate these elements at the target levels.

Phase II methods for organics generally consist of quantitative GC methods, which are modified versions of USEPA 600 and 8000 series methods. The Phase II analytes include those covered in Phase I as well as additional analytes recommended for inclusion based on the Phase I study (see Section 3.1). A comparison of the Phase I and II analytical techniques and reporting limits is given in Table 3.2-2.

3.3 Limits of Quantitation

There are two limits of quantitation, an upper and a lower. These limits represent the concentration ranges where the presence of compounds can be quantified. For the RMA RI program, a lower limit of quantitation has been designated as the certified reporting limit (CRL). This estimate for each analyte is numerically and philosophically different from the method detection limit (MDL) estimated by USEPA protocols. Specifically, the CRLs tend to be numerically larger values than the MDLs for the same analytical methodologies and sample matrices. This is not to imply that one estimate is correct and one is incorrect; they are

Table 3.2-2 Phase I and II Analytes and Reporting Limits for RMA Soil Samples, Selected Laboratories (page 1 of 4)

	PHASE I					PHASE II			
	REPORTING LIMITS (ug/g)					REPORTING LIMITS (ug/g)			
Analyte	Method	CAL	ESE	MRI	DataChem	Method	CAL	ESE	DataChem
Volatile	GC/MS								
Bicycloheptadiene		0.3	0.3	0.8	0.4	GC/FID	-	5.1	1.1
Dicyclopentadiene		0.3	0.3	0.3	0.7		-	5.1	0.45
Methylisobutylketone		0.3	0.5	0.4	0.7		-	5.2	0.64
Carbon tetrachloride	GC/MS	0.3	0.3	0.4	0.3	GC/HECD	-	0.052	0.12
Chlorobenzene		0.3	0.3	0.3	1.0		-	0.051	0.20
Chloroform		0.3	0.3	0.7	0.3		-	0.052	0.068
1,1-Dichloroethane		0.9	0.3	0.5	2.0		-	0.049	0.074
1,2-Dichloroethane		0.3	0.3	0.4	0.6		-	0.050	0.085
1,1-Dichloroethene		-	-	-	-		-	0.047	0.24
trans-1,2-Dichloroethene		0.3	0.3	0.8	2.0		-	0.051	0.26
Methylene chloride		0.7	0.3	-	2.0		-	0.50	3.7
Tetrachloroethene		0.3	0.3	0.5	0.3		-	0.051	0.27
1,1,1-Trichloroethane		0.3	0.3	0.5	0.4		-	0.049	0.088
1,1,2-Trichloroethane		0.3	0.3	0.6	0.4		-	0.050	0.26
Trichloroethene		0.3	0.3	0.6	0.5		-	0.050	0.14
Benzene		0.3	0.3	1.0	0.3	GC/PID	-	0.081	0.085
Ethylbenzene		0.3	0.3	0.4	0.4		-	0.043	0.16
Toluene		0.3	0.3	0.3	0.3		-	0.096	0.19
m-Xylene		0.7	0.3	0.3	0.8		-	0.053	0.26
o- and p-Xylenes*		0.3	0.5	0.5	5.0		-	0.086	0.39
Dimethyldisulfide		0.8	0.3	4.0	20.	GC/FPD	-	0.70	-
Dibromochloropropane		0.4	0.3	0.9	2.0	GC/EC	0.014	0.005	0.005

Table 3.2-2 Phase I and II Analytes and Reporting Limits for RMA Soil Samples, Selected Laboratories (page 2 of 4)

	PHASE I					PHASE II		
	REPORTING LIMITS (ug/g)				REPORTING LIMITS (ug/g)			
Analyte	Method	CAL	ESE	MRI	DataChem	Method	CAL	ESE	DataChem
Semi-Volatile									
Atrazine	GC/MS	0.3	0.7	0.5	0.3	GC/NPD	-	0.25	-
Malathion		0.3	0.6	2.0	0.7		-	0.25	-
Parathion		0.4	0.7	2.0	0.9		-	0.25	-
Supona		0.3	0.5	0.9	0.6		-	0.25	-
Vapona		0.3	0.3	0.3	3.0		-	0.70	-
Aldrin		0.3	0.9	0.5	0.3	GC/EC	-	0.05	0.002
Chlordane		0.6	1.0	6.0	2.0		-	0.20	0.023
p,p'-DDE		0.3	0.3	0.5	0.6		-	0.053	0.002
p,p'-DDT		0.6	0.4	2.0	0.5		-	0.050	0.002
Dieldrin		0.3	0.3	0.6	0.3		-	0.051	0.003
Endrin		0.3	0.7	4.0	0.5		-	0.060	0.006
Hexachlorocyclopentadiene		0.3	1.0	1.0	0.6		-	0.051	0.002
Isodrin		0.3	0.3	0.6	0.3		-	0.053	0.001
Dibromochloropropane		0.3	0.3	0.6	0.3	GC/EC	0.014	0.005	0.005
Diisopropylmethyl-phosphonate		0.3	0.5	0.3	1.0	GC/FPD	0.050	0.11	-
Dimethylmethylphosphonate		-	2	3	-		0.050	0.11	
Benzothiazole		-	-	-	-	GC/FPD	-	0.53	-
Chlorophenylmethyl Sulfide		4.0	0.3	0.3	0.9		-	1.1	-
Chlorophenylmethyl Sulfone		0.6	0.3	0.4	0.3		-	2.4	-
Chlorophenylmethyl Sulfoxide		7.0	0.4	1.0	0.3		-	2.3	-
Dimethyldisulfide		-	-	-	-		-	0.70	-
1,4-Dithiane		7.0	0.3	2.0	0.4		-	0.60	-
1,4-Oxathiane		6.0	0.3	0.5	0.3		-	0.90	-

Table 3.2-2 Phase I and II Analytes and Reporting Limits for RMA Soil Samples, Selected Laboratories (page 3 of 4)

		PHASE I REPORTING LIMITS (ug/g)				PHASE II REPORTING LIMITS (ug/g)			
Analyte	Method	CAL	ESE	MRI	DataChem	Method	CAL	ESE	DataChem
Metal									
Mercury	CVAA	0.06	0.05	0.07	0.0	CVAA	0.060	0.050	0.050
Arsenic	GFAA	5.0	4.7	2.5	2.5	GFAA	5.0	4 7	2.5
Cadmium	ICP	0.66	0.90	0.51	0.74	ICP	0.66	0.90	0.74
Chromium		5.2	7.2	7.4	6.5		5.2	7.2	6.5
Copper		4.9	4.8	4.9	4.7		4.9	4.8	4.7
Lead		13.	17.	16.	8.4		13.	17.	8.4
Zinc		9.5	16.	28.	8.7		9.5	16.	8.7
Other									
n-Nitrosodimethylamine		-	-	-	-	GC/NPD	-	-	0.26
n-Nitrosodi-n-propylamine		-	-	-	-		-	-	0.10
Chloroacetic acid		-	-	-	-	HPLC	-	18.	35.
Thiodiglycol		-	-	-	-		-	2.6	4.2
Isopropylmethylphosphonic Acid		-	-	-	-	HPLC	4.7	2.6	-
Isopropylmethylphosphonic Acid		-	-	-	-	IONCHROM	-	2.1	-
Fluoroacetic Acid		-	-	-	-		-	2.0	-
Methyl Phosphonic Acid		-	-	-	-		-	2.0	-
Chloride	IONCHROM	-	16.	-	14.	IONCHROM	-	16.	
Fluoride		-	4.5	-	10.		-	4.5	10
Sulfate		-	95.	-	88.		-	95.	88.
Hydrazine		-	-	-	-		-	-	50
Methylhydrazine		-	-	-	-		-	-	200
Unsymmetrical Dimethyl Hydrazine		-	-	-	-		-	-	200
Dilsopropylamino-ethanethiol[1]		-	-	-	-		-	-	-
Dimethyl Arsenous Acid[1]		-	-	-	-		-	-	-
Tributylamine[1]		-	-	-	-		-	-	-

Table 3.2-2 Phase I and II Analytes and Reporting Limits for RMA Soil Samples, Selected Laboratories (page 4 of 4)

NOTE:

[1] Certification for this analyte has not yet been received by any laboratory.

- Certification was not received.

* Ortho- and para- (o- and p-) xylenes coelute under the GC conditions specified in this method.

Laboratory

CAL - California Analytical Laboratory, W. Sacramento, California
ESE - Environmental Science and Engineering, Inc., Gainesville, Florida
MRI - Midwest Research Institute, Kansas City, Missouri
DataChem - Formerly UBTL, Salt Lake City, Utah

Method

GC/MS - gas chromatography/mass spectrometry
GC/FID - gas chromatography/flame ionization detector
GC/HECD - gas chromatography/Hall electrolytic conductivity detector
GC/PID - gas chromatography/photoionization detector
GC/FPD - gas chromatography/flame photometric detector
GC/EC - gas chromatography/electron capture
GC/NPD - gas chromatography/nitrogen phosphorus detector
CVAA - cold vapor atomic absorption
GFAA - graphite furnace atomic absorption
ICP - inductively coupled plasma
HPLC - high performance liquid chromatography
IONCHROM- ion chromatography

based on different assumptions and risks as described in the following sections.

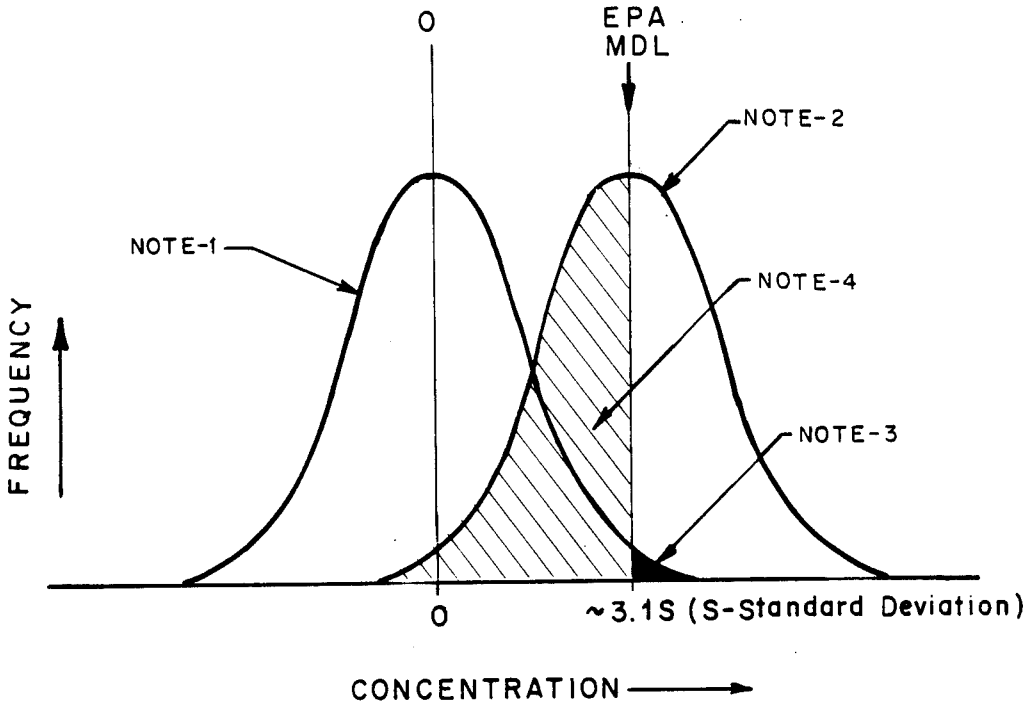
3.3.1 USEPA Method Detection Limit

The USEPA method detection limit (MDL), as defined in 40 CFR Part 136, Appendix B (1984), is the "minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte." The procedure for determining the method detection limit (MDL) is presented in Appendix B of 40 CFR 136. A copy of this Federal Register excerpt is reproduced in Appendix A.

To obtain an USEPA MDL, it is first necessary to estimate the detection limit based on one of several instrument responses and prior experience of the analyst. A solution is then spiked at a concentration corresponding to 1 to 5 times the estimated method detection limit. A minimum of seven replicate determinations are then performed by processing each through the entire analytical procedure. A separate blank measurement is made for each sample and the average blank measurement is subtracted from sample measurements. The standard deviation is calculated from these replicate measurements and the MDL is estimated by multiplying the standard deviation by the Student's t-value

corresponding to n-1 degrees of freedom and a 99 percent confidence level. For seven replicates (six degrees of freedom), the t-value is 3.143. Figure 3.3.1-1 offers a graphical depiction of these relationships. Note that normal distributions are assumed for both blank and sample measurements. It is also assumed that the variances for both blank and sample measurements are equal. In reality, both of these assumptions are frequently violated but the error introduced is usually minor compared to the overall uncertainties.

In all decisions related to the detection of trace analytes, traditional techniques have only considered protection against Type I errors, i.e., reporting an analyte as present when it is not. An equally serious but often ignored problem is the Type II error, i.e., reporting an analyte as absent when it is present (see Figure 3.3.1-1). The statement that an MDL represents 99 percent confidence is based solely on the Type I error. If the true concentration in a sample is equal to the MDL, the risk of claiming that the analyte is absent is 50 percent. In other words, for samples with concentrations equal to the MDL, half will be reported as present and half will be reported as absent. (It could also be noted that the use of an average blank correction excludes normal blank variability and further aggravates the Type II error because the MDL is overly opti-



EXPLANATION

NOTE-1 – DISTRIBUTION OF BLANK MEASUREMENTS

NOTE-2 – DISTRIBUTION OF MEASUREMENTS WITH A MEAN CONCENTRATION EQUAL TO THE MDL.

NOTE 3 – TYPE I (α RISK) ERROR = 1%, ie RISK OF CLAIMING DETECTION WHEN TRUE CONCENTRATION IS ZERO.

NOTE 4 – TYPE II (β RISK) ERROR = 50%, ie RISK OF CLAIMING ABSENCE WHEN TRUE CONCENTRATION IS = MDL

GRAPHICAL ILLUSTRATION OF EPA METHOD DETECTION LIMIT (MDL)

PREPARED FOR U.S. ARMY PROGRAM MANAGER'S OFFICE FOR ROCKY MOUNTAIN ARSENAL

ABERDEEN PROVING GROUND, MD.

FIGURE 3.3.1-1

mistic.) Needless to say, such findings lead to excessive noise in spatial distribution maps.

3.3.2 USATHAMA Certified Reporting Limit

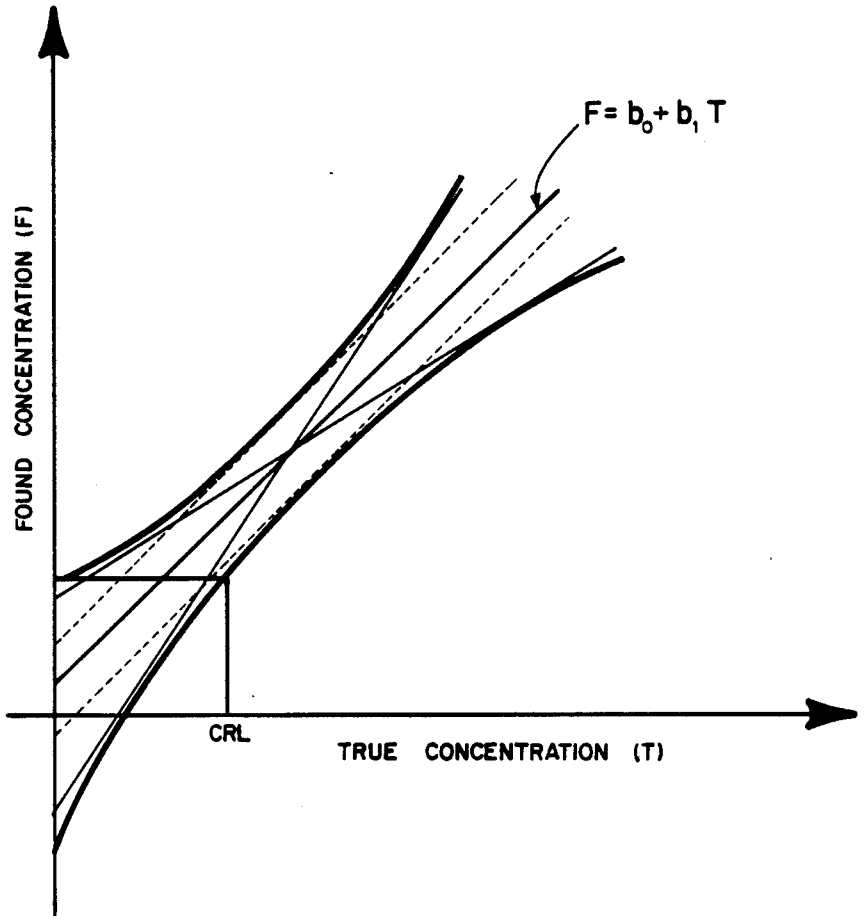
For CRLs as described by USATHAMA, the estimate is based on a 90 percent confidence band (for individual measurements) about a linear regression equation determined for a plot of found concentrations versus taken concentrations. After a target reporting limit (TRL) has been chosen, spike additions are made at concentrations ranging from 0.5 times the TRL to 10 times the TRL. This is the standard USATHAMA protocol; however, for the RMA program, this procedure was supplemented. Where concentrations were expected to be high, an additional three spikes per concentration order of magnitude increase were made. This removes the necessity of diluting the sample when concentrations are high. The elimination of additional diluting requirements helps to control sources of variability in the analytical procedure. Found concentrations are determined for each spike concentration on each of four days using the complete analytical procedure.

A plot of found versus taken concentrations is tested against the theoretically expected linear model through the origin. When the requirement of a linear model through the origin is not met, the highest concentration values are

systematically eliminated from the calculations until these requirements are satisfied. The CRL is based on the joint uncertainties of the "best-fit" slope and intercept regression constants as illustrated in Figure 3.3.2-1. At least one of the tested concentrations must be below the CRL, otherwise the lowest tested concentration is the CRL. Details of the computations are given in Section 4.8.2 of USATHAMA QA Program, 1987. This section is reproduced in Appendix B.

Although it is not possible to accurately specify the Type I error for the CRL, it should be very small. As stated above, the CRL is determined from the joint uncertainties of the slope and intercept regression. It is based on a series of measurements and not the distribution of measurements about a concentration of zero.

As with all detection decisions, there is Type II risk associated with the use of CRLs. For a concentration equal to the CRL, there is once again a 50 percent chance of reporting it as not detected, i.e., below the CRL. In that respect, the risk is seemingly no different than it is for the MDL. However, there clearly is a concentration range below the CRL where signals are still detected (region A in Figure 3.3.2-2(b)). The requirement for at least one of the tested concentrations to be below the CRL ensures this situation. This region has been described by many as the region of detection where uncertainties are too large to justify



EXPLANATION

THE CRL IS THE VALUE OF T CORRESPONDING TO A POINT ON THE LOWER CONFIDENCE BAND WHERE THE VALUE OF F EQUALS THE VALUE OF F AT T=0 ON THE UPPER CONFIDENCE BAND.

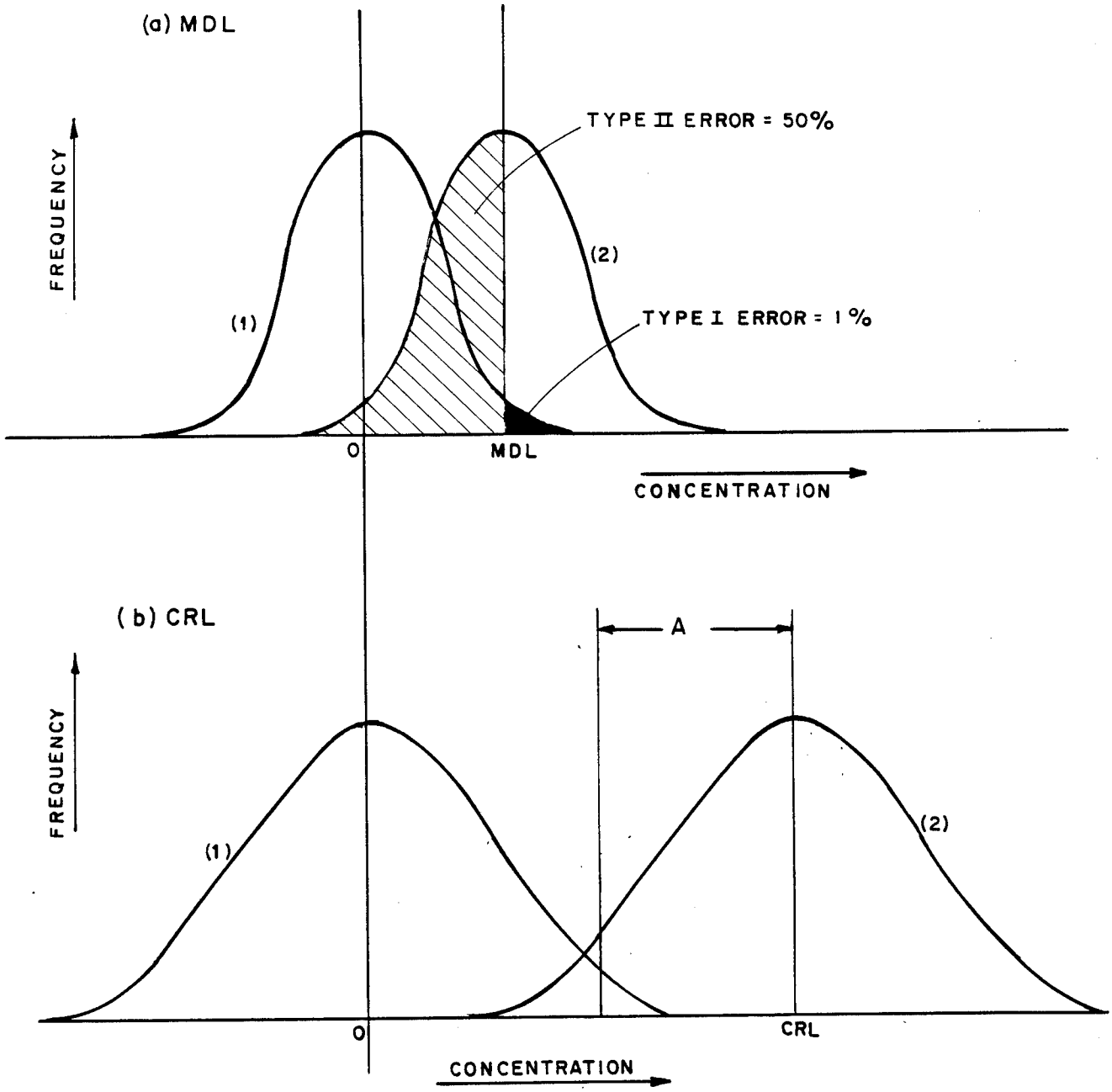
THE CURVED CONFIDENCE BANDS REPRESENT THE JOINT INCERTAINTIES IN THE SLOPE (b_1) AND INTERCEPT (b_0)

GRAPHICAL ILLUSTRATION OF USATHAMA CERTIFIED REPORTING LIMIT (CRL)

PREPARED FOR U.S. ARMY PROGRAM MANAGER'S OFFICE FOR ROCKY MOUNTAIN ARSENAL

ABERDEEN PROVING GROUND, MD.

FIGURE 3.3.2-1



EXPLANATION

(1)- DISTRIBUTION OF BLANK MEASUREMENTS

(2)- DISTRIBUTION OF MEASUREMENTS WITH A MEAN CONCENTRATION EQUAL TO THE MDL (a) OR THE CRL(b)

A – THE CONCENTRATION RANGE WHICH WILL PRODUCE DETECTABLE SIGNALS BUT OF INSUFFICIENT MAGNITUDE TO JUSTIFY QUANTITATIONS.

COMPARISON OF MDL AND CRL

PREPARED FOR U.S. ARMY PROGRAM MANAGER'S OFFICE
FOR ROCKY MOUNTAIN ARSENAL
ABERDEEN PROVING GROUND, MD.

FIGURE 3.3.2-2

quantitation. Although these highly uncertain results are not sent to the RMA data management system, they are available as raw data to supplement reported results where there may be ambiguities or contradictory analyses.

It must be recognized that the dispersions for MDL and CRL determinations shown in Figure 3.3.2-2 are reasonable estimates on a relative basis but they are not based on actual data. For CRLs, Type I risks are difficult to specify because the CRL is not anchored to a concentration of zero. Thus, the location of the lower concentration boundary of region A is only an estimate.

3.3.3 Comparison of MDL and CRL

The relationship of CRL to MDL is illustrated in Figure 3.3.2-2. The dispersion of the distributions will usually be greater for CRL than for MDL determinations because (a) the estimated standard deviation includes normal variability associated with day-to-day variations, (b) the standard deviation is a pooled estimate based on concentrations which cover the range to be expected for real samples (standard deviations often tend to increase somewhat as concentration increases although variances are frequently homogeneous over the calibrated range), and (c) the uncertainties in the calibration function are included in the CRL estimate. The use

of this larger but more comprehensive estimate of the standard deviation is one major reason why CRLs are normally larger than MDLs for the same analytical procedure. We believe that the CRL estimates from the USATHAMA procedure are better representations of what will be achieved in long-term programs conducted by contractor laboratories. These are most appropriate for the objectives and the constraints of the RMA RI program.

3.4 Quality Assurance/Quality Control

The Quality Assurance/Quality Control (QA/QC) procedures for the laboratory analysis of RMA samples was designed to ensure the production of valid and properly formatted data for use in litigation. The QA procedures specified adhere to USATHAMA requirements. The precision, accuracy, and sensitivity of each method used during the sampling and analysis efforts at RMA were considered in the development of the RMA RI program. The specific objectives of the QA/QC program are as follows:

- Ensure adequate precision and accuracy for measurement data;
- Ensure validity of procedures and systems used to achieve project goals;
- Ensure that the documentation is verified and complete;
- Quickly identify deficiencies affecting the quality of data;

- Perform corrective actions that are approved and properly documented;
- Ensure that the data acquired will be sufficiently documented to be legally defensible;
- Ensure that the precision and accuracy levels attained during the USATHAMA analytical certification program are maintained during the project; and
- Ensure adherence to established USATHAMA QA Program guidelines and standards, including those requirements directed in the AMSMC-PCB (A) letter dated April 30, 1985 from James K. Warrington.

Inherent in the QA/QC program is laboratory certification. Before any of the RMA samples are submitted to a laboratory for analysis, the laboratory must demonstrate its ability to perform the analysis with acceptable reliability. Laboratory certification ensures that the QA/QC requirements can be met. The laboratories must receive certification for each analyte and for each technique. For example, the laboratories receive two certifications for benzene, GC/MS (Phase I) and GC/PID (Phase II). Hence, the certification of Phase I methods does not guarantee Phase II certification. Details regarding the laboratory certification process are given in Section F of USATHAMA QA Program.

Specific QA/QC procedures for the RMA program are summarized below. These requirements are extensive. Laboratory control samples are introduced into each lot of actual samples. For all volatile and semi-volatile compounds analyzed using GC/MS, a blank and a QC surrogate spike are run

with each lot. In addition, all field samples are spiked with surrogate compounds to help determine possible matrix interferences. Duplicate high concentration spikes and a low concentration spike are employed for all non-GC/MS analyses. The designation of a lot size is determined by the rate limiting step in an analysis and can be either the preparation of the sample for analysis or the actual determination of the analyte concentration. The rate limiting step for GC/MS work is the instrumentation, while for ICP and AA analyses it is the sample preparation.

Data from the analysis of these control samples are compiled and control charts are prepared. For GC/MS methods and all unreplicated spikes, 3-day moving average control charts are used. For replicated spikes, Standard Shewhart $\bar{X}$ and R charts are used. The control chart limits are updated daily for the first 20 in-control lots and after each additional 20 control lots using the past 40 in-control lots. QC charts are kept daily by the laboratories and these are submitted weekly to the Analytical Branch of the Technology Division of USATHAMA for final review. The laboratory is responsible for daily QC. If the QC sample results should indicate that values are outside the established control limits for a particular lot, further analysis is stopped until adjustments to the procedures are made to bring results back into control.

Audits of the laboratories are performed quarterly to confirm that they are adhering to the specified QA/QC procedures. These audits include meeting with laboratory personnel, review of the data packages (including QA/QC data), and discussions of existing and/or potential problems and how they were solved. Information regarding the efficiency of the analytical procedures is shared among the laboratories. A program in which such cooperation exists among contractor laboratories is unusual. The laboratories are competitors and these question-and-answer sessions could be considered to be revealing trade secrets. The level of cooperation indicates that these laboratories are dedicated to the efficient and timely completion of the RMA remedial investigation.

4.0 PROGRAM EVALUATION

The RMA remedial investigation analytical methodologies will be evaluated in this section. The evaluation will provide the information necessary to suggest whether the Phase I and Phase II certified reporting limits (CRLs) can and should be lowered. In addition, the QA/QC program will be compared with standard QA/QC protocols, including those specified by the USEPA under their Contract Laboratory Program (CLP). The program evaluation will not consider the benefit or liability of changes to the current program.

4.1 Method Certified Reporting Limit

Detection limits are the interactive product of many variables such as (a) the analytical method, (b) the instrumentation, (c) the samples, and (d) the analyst. They are not fundamental constants. Detection limits can be "managed" in various ways. Variables such as sample size, extent of preconcentration, risks in decision making, and purity of reagents can often be adjusted. However, each of these factors is constrained by practical considerations. For example, increased preconcentration of extracts can compromise detection capability because interferents are concentrated at the same rate as the analytes and the analyte signal-to-noise ratio actually deteriorates. It is also important to recognize that increasing the complexity of analytical procedures increases the risk of inaccurate results.

Another aspect of "managing" detection limits relates to the design of the experiment from which the detection limit estimates are extracted. MDLs are based on several replicate measurements on aliquots of a single sample with a concentration close to the detection limit. No allowance is made for day-to-day variability or for calibration over a range of concentrations expected in field samples. However, in actuality, samples are analyzed over an extended period and often by several contractors. If quantitative analyses are desired, it is necessary to distribute the standards

over the range to be calibrated rather than to focus all of the effort on the lowest detectable concentration. Since the high concentration sites represent the greatest risk, it is appropriate to maximize the effort to ensure accurate results over the entire concentration range of concern.

In light of the above, RMA policy has been dedicated to produce quantitative data of high credibility so that seriously contaminated sites can be clearly delineated and an effective cleanup strategy can be planned. Very conservative (in terms of risk) CRLs have been employed to ensure that reliable quantitative estimates can be generated. Inclusion of all major sources of random variability in the reproducibility estimates were a deliberate attempt to anticipate the actual variabilities that would be present in a long-term program.

Lower concentrations could have been reported. However to do so would have required (a) taking greater risks with respect to the validity of the numbers, (b) conducting specific and detailed calibrations in the region of the detection limit at the expense of less effort to calibrate in the region of elevated concentrations, or (c) using more specific methods that would have precluded the broad survey capabilities for nontarget compounds that were available with the methods chosen. None of these alternatives was acceptable for Phase I. During Phase II, item (c) above has

been implemented for several analytes demonstrated to be present during Phase I.

The above does not indicate that either MDLs or CRLs are incorrect. It simply means that they are based on different assumptions and different experimental designs. The former are suitable for limited time studies where only qualitative data are required. For RMA, we believe that the CRLs were and continue to be a proper choice of available technology, and are the most appropriate for the RMA program.

4.2 Evaluation of Quality Assurance/Quality Control

This evaluation of the QA/QC employed for the RMA remedial investigation consists of two parts. The first consists of a comparison of USATHAMA, USEPA Contract Laboratory Program (CLP) and the Navy Assessment and Control of Installation Pollutants (NACIP) QA programs. This comparison is not intended to indicate one program as correct and the remaining as incorrect or deficient, rather, it will present the differences among the programs. The second part of this review is an evaluation of the performance of the RMA QA/QC program.

The USATHAMA QA/QC program is compared to the similar programs directed by other federal agencies. The two pro-

grams selected were the USEPA Contract Laboratory Program, and the QA Guide for Navy Assessment and Control of Installation Pollutants (NACIP) Program. The USEPA program was selected because it is considered a state-of-the-art program and the NACIP Program was selected because it is administered by another branch of the U.S. Department of Defense. Table 4.2-1 compares major issues addressed in laboratory QA/QC programs and illustrates similarities and differences in the programs.

As the table indicates, the USATHAMA QA/QC requirements are similar to those specified by the USEPA for lot size, control samples, and calibration frequency. The lot size required by the two programs, although addressed differently, results in producing the number of field samples that can be analyzed as a single unit. The number of control samples per lot are similar, except that the USATHAMA program requires one more standard matrix spike for gas chromatographic analysis. Instrument calibration is required after every 12-hour period for the USEPA program, whereas the USATHAMA program also prescribes use of USEPA's guidelines.

The USATHAMA program is more specific in addressing out-of-control analyses, reporting levels, and statistical review. USATHAMA provides all of its contractor laboratories with software for statistical analysis and has a data

Table 4.2-1. Comparison of USATHAMA, USEPA, and NACIP Quality Assurance/Quality Control Requirements.

Activity	USATHAMA	USEPA	NACIP
Lot Size			
	Defined as: 1) Not to exceed 24-hour analysis period 2) Must be same matrix 3) Must not exceed limiting step of extraction process	Defined as: 1) - Each case received, or - 20 field samples per case, or - 14 days, or - samples of similar concentration, whichever is less	1) To be addressed by laboratory in QA/QC plan
Control Samples Per Lot			
Matrix Method Blank(s)	1) One	1) One	1) To be addressed by laboratory in QA/QC plan a) To be addressed in monthly progress report
Standard Matrix Spike(s)	1) One at 2 CRL* 2) Two at 10 CRL*	1) Two at expected concentration	
Surrogate Spike (GC/MS only)	1) All samples, blanks, and spikes	1) All samples, blanks, and spikes	
Instrument Calibration			
Frequency	1) Must meet or exceed manufacturer's recommendations	1) Every 12-hour period	1) To be addressed by laboratory in QA/QC plan

Table 4.2-1. Comparison of USATHAMA, USEPA, and NACIP Quality Assurance/Quality Control Requirements.

Activity	USATHAMA	USEPA	NACIP
Out of Control Analysis			
Methods used	1) Calibration curves 2) Spike/Surrogate recovery A) X control chart analysis B) R control chart analysis 3) Low concentration spike analysis 4) Exceed sample holding times 5) Improper sample collection/ preservation 6) Record keeping omissions	1) Calibration curves 2) Analysis acceptance criteria A) Matrix spike recovery B) Surrogate spike recovery C) Method blank analysis D) Matrix spike duplicates	1) To be addressed by laboratory in QA/QC plan A) Must be addressed in monthly progress report
Required Statistical Review			
	1) Software provided by USATHAMA to assess precision and accuracy of analysis 2) USATHAMA maintains data management system to automate statistical analysis	1) Contract specifies equations to assess precision and accuracy of analysis	1) To be addressed by laboratory in QA/QC plan

CRL* = Certified Reporting Limit

Based on
1) USATHAMA QA Program Manual
2) USEPA Contract Laboratory Program Manual
3) Sampling and Chemical Analysis QA Guide for Navy Assessment and Control of Installation Pollutants (NACIP) Program prepared by Naval Environmental Protection Support Service

management system to store all of this information. The USEPA specifies equations to be used in a statistical analysis of the laboratory data. The limits of quantitation are different for each of the two programs; these differences have been discussed in Section 3.3 of this report.

The Navy program relies on the contracted laboratory to specify how it will address QA/QC with their submission of a QA/QC plan. The Navy then makes a judgment as to whether the laboratory includes appropriate controls. After a contract is placed, the Navy tracks the laboratory by reviewing monthly progress reports.

A comparison of the USATHAMA QA programs and the USEPA CLP was also made by Oak Ridge National Laboratory. This comparison was based on the USEPA's Sixteen Point QA project plan. The sixteen points follow the program from the stating of the description and objective, to the sample collection and analysis, then finally through the preparation of the reports. Pertinent sections of this comparison are reproduced in Appendix C. Those included are QA objectives for measurement data, calibration procedures and frequency, data reduction, validation and reporting, and internal quality control charts.

As stated previously (Section 3.3 of this report) throughout the RMA RI, control charts are developed and

maintained to monitor the accuracy and precision of the analytical procedures. These charts are used to help detect problems with the method before data of unacceptable quality are produced. This allows the daily check of quality control to be the responsibility of the laboratory and in particular, the analyst. Out-of-control situations can be remedied without large amounts of down time. This aspect of the analytical program is unique to the RMA RI. The efficiency of the program is enhanced by giving this responsibility to the laboratories. As stated in Section 3.3, the quality-control program requires the spiking of surrogates onto a reference soil sample. The volatile and semivolatile surrogate compounds are spiked at low concentrations. For the metals analysis, analytes are spiked at low and at high concentrations.

The range of acceptable individual percent recoveries was determined for surrogates and for the spiked metal analytes added to the reference soil as summarized in Table 4.2-2. The values represent ± 3 sigma deviations from the mean. Two ranges of values are given for each category. The first represents the values from recent analyses in 1986, and the second set of values are from the original data sets in 1984 to 1985. These values demonstrate that the performance of the laboratories has improved as the program has progressed. For every case, except arsenic high spikes, the new limits are tighter than the originals. In

Table 4.2-2. Range of Acceptable Individual Percent Recoveries of RMA Control Sample Performance, Phase I Analyses.

Analyte	Low Spikes		High Spikes	
	Recent[1]	Original[2]	Recent[1]	Original[2]
Methylene Chloride-d2	68% - 132%	(57% - 132%)		
1,2-Dichloroethane-d4	75% - 125%	(70% - 128%)		
Ethylbenzene-d10	77% - 127%	(73% - 125%)		
2-Chlorophenol-d4	50% - 110%	(38% - 109%)		
1,3 Dichlorobenzene-d4	45% - 111%	(34% - 101%)		
Diethylphthalate-d4	68% - 113%	(51% - 114%)		
Di-n-octylphthalate-d4	52% - 136%	(40% - 144%)		
Cadmium	76% - 119%	(66% - 124%)	85% - 106%	(82% - 111%)
Copper	65% - 119%	(60% - 119%)	83% - 105%	(81% - 104%)
Chromium	64% - 133%	(63% - 137%)	82% - 104%	(81% - 108%)
Lead	63% - 115%	(56% - 134%)	81% - 103%	(78% - 108%)
Zinc	74% - 114%	(68% - 125%)	84% - 103%	(81% - 109%)
Mercury	76% - 130%	(71% - 129%)	90% - 116%	(85% - 118%)
Arsenic	67% - 117%	(64% - 117%)	76% - 116%	(80% - 114%)

[1] Recoveries based on recent data, 1986.
[2] Recoveries based on original data sets, 1984-1985.

These values were derived from the mean recovery of all laboratories plus or minus three standard deviations ($X \pm 3$ s.d.).

general, the greatest improvements are in the lower boundary. The values indicate that the performance of the contractor laboratories is good, and this reflects well on the appropriateness and applicability of the USATHAMA QA program.

4.3 Improved Analytical Procedure

During the course of the remedial investigation, the potential for lowering CRLs of soil and sediment analyses for organochlorine pesticides (i.e., aldrin, dieldrin, and endrin) was investigated. This possibility was raised after the review of a Waterways Experiment Station (WES) report. The report ("Upper and Lower Derby Lakes and Gun Club Pond Sediment Investigation" by T. E. Meyers and P. A. Spaine of WES, June 1983) stated that detection limits used in the WES study were 1 micrograms per kilogram (ug/kg) for aldrin and dieldrin and 1.0 ug/kg for endrin (0.2 ug/kg was stated in the report, but this was later revised to 1.0 ug/kg) analyses. The 1986 certified reporting limits for the RMA RI were 53 ug/kg for aldrin, 85 ug/kg for dieldrin, and 170 ug/kg for endrin.

Although method detection limits are generally lower than CRLs (as stated in Section 3.3 of this report), the procedures for these analyses were reviewed to determine if

lower CRLs could be certified. The USATHAMA method was modified such that the concentration factor was increased to 1 gram soil/mL extract from 0.05 gram soil/mL extract. This corresponds to the lowering of the CRL to 2 to 10 ug/kg for the three analyses (see DataChem CRLs). Table 3.2-2 presents the actual CRLs for aldrin, dieldrin, and endrin (Lessley, 1987).

The CRLS for the remaining methods were also reviewed. It was determined that they could not be lowered further (Blose, 1987).

5.0 SUMMARY

As part of the remedial investigation program at RMA, a review of the analytical chemical program has been made to assess the compatibility of the program with remedial investigation goals. The main objective of the remedial investigation is to define the areal and vertical extent of contamination in all media as well as to assess the potential for migration.

To provide data to define the spatial distribution of RMA contamination, the analytical program for the remedial investigation had to (a) identify chemical elements or compounds known to be present at RMA, (b) provide reliable analytical results over a large range of concentrations, (c)

follow established methods closely enough to allow the intercomparison of data generated at several commercial laboratories with reasonable analytical turnaround, and (d) meet the quality assurance and quality control goals specified by USATHAMA.

The following observations are based upon this Phase I and II program evaluation:

1) The certified reporting limits incorporated in the USATHAMA protocol are appropriate to the program (i.e., sample numbers, concentration ranges, and sensitivities).

2) The analytical scheme has produced a large mass of results that meets rigorous tests of quality assurance and quality control and also adheres to the remedial investigation schedule.

3) Analytical methodologies for target organic compounds using GC/MS have also provided for the detection of nontarget compounds not identifiable with other standard analytical techniques.

4) Laboratory performance under the auspices of the quality assurance and quality control program has

improved such that tighter control limits for the analyses are now being attained.

5) The analytical methodology for the analysis of organochlorine pesticides was reviewed and revised and new lower certified reporting limits were incorporated into the analytical program.

It is the opinion of the program manager for Rocky Mountain Arsenal that the analytical chemistry program supporting the Rocky Mountain Arsenal remedial investigation is consistent with CERCLA, SARA, and the NCP, and within the constraints of this program. The determination of the analytical methodologies used in the RMA soil investigation and its supporting documents are appropriate for the program's goal of defining the areal and vertical extent of contamination at Rocky Mountain Arsenal.

6.0 REFERENCES

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APPENDIX A

Federal Register excerpt, Appendix B to Part 186 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11

Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 / n\right]$$

$$S = (S^2)^{1/2}$$

where:

X_i; i=1 to n, = are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha=0.99)} \quad (S)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha=.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike in the matrix at the calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the others into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B < 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S^2_A + 6S^2_B}{12}\right]^{1/2}$$

if $S^2_A/S^2_B > 3.05$, respike at the most recent calculated

MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

MDL = 2.681 (S_{pooled})

where 2.681 is equal to $t_{(12, 1-\alpha = .99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL

UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	10	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

Appendix C to Part 136—Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 *Interference check sample*—A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)

3.9 *Quality control sample*—A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3).

3.10 *Calibration standards*—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

3.11 *Linear dynamic range*—The concentration range over which the analytical curve remains linear.

3.12 *Reagent blank*—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2)

3.13 *Calibration blank*—A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 7.5.1)

3.14 *Method of standard addition*—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 10.6.1.)

4. Safety

4.1 The toxicity of carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is repsonsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [14.7, 14.8 and 14.9] for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 *Spectral interferences* can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from

APPENDIX B

USATHAMA QA Program excerpt, Section 4.8.2
Certified Reporting Limit (CRL)

The statistical calculations compare the found concentration of the standard spiked samples with the known target spiked concentration. The found concentrations must have been determined from calibration curves constructed according to the standardized method. Method blank and recovery factors shall not be used to correct found concentrations used during analysis of certification data. The calculations must be performed for each target analyte in a method. The reported found concentrations and statistical analysis values obtained during Class 1, Class 1A, and Class 1B certification activities should use at most three significant figures.

4.8.1 Lack of Fit (LOF) and Zero Intercept (ZI) Tests

Data obtained during certification analyses shall be tested for linearity using the LOF and ZI tests (Appendix E). All data must have been collected during periods when instrumental calibration was in control (within 10% of the mean response for inorganics analyses in surface/groundwaters and within 25% of the mean response for all other analyses). Data obtained from valid methods using properly calibrated instruments are expected to be linear and have a zero intercept, when found concentrations are compared to the target concentrations. This relationship must be tested because calculation of the CRL assumes a linear relationship.

Data from each of the four days (Class 1 and Class 1B) or single day (Class 1A) of certification analyses shall be pooled and tested for LOF. All LOF test calculations and results shall be included in the Performance Data Package. If the pooled data fails the LOF test at the 95% confidence level, the USATHAMA Project Officer must be contacted for discussion and guidance.

4.8.2 Certified Reporting Limit (CRL)

Before any analytical system is employed in a survey, sufficient spikes and blanks will be run to statistically establish the lowest sample concentration which may be reported. This concentration is the CRL. For USATHAMA IR projects, CRL's shall be determined by using the USATHAMA program with 90% confidence limits. This CRL is associated with the entire method and reflects all sample preparation and measurement steps. Contractors are cautioned about two items. First, this approach differs from instrumental detection limit (e.g., three times the blank signal to noise ratio); the method CRL will likely be considerably higher than the instrumental detection limit. Second, because the CRL reflects use of the entire method, all steps of all analyses must always be performed in exactly the same way.

The CRL is derived from the following assumptions:

- The relationship between the found concentration and target concentration is linear;

- The variance about the least squares linear regression line is homogeneous over the tested concentration range; and
- Found concentrations for a given target concentration are normally distributed.

Based on these assumptions, the least squares linear regression line of the form,

(1) $Y = Y_o + bX$

is determined, where:

Y = Found concentration;

Y_o = Y axis (found concentration) intercept;

b = Slope of the line; and

X = Target concentration.

The certification performance data (X,Y paired data) are used to determine the least squares regression line according to the following formula, which assume that errors occur only in the found concentration:

(2) $$\text{Slope} = b = \frac{N\Sigma X_i Y_i - \Sigma X_i \Sigma Y_i}{N\Sigma X_i^2 - (\Sigma X_i)^2}$$

where:

N = Number of data points;

X_i = The i-th target concentration; and

Y_i = The i-th found concentration.

(3) $$\text{Y Axis Intercept} = Y_o = \frac{\Sigma Y_i - b\Sigma X_i}{N}$$

where:

b = Slope of the least squares linear regression line, from Equation 2.

The upper confidence limit about the regression line is given by:

$$(4) \qquad Y = Y_o + bX + S_{Y.X}\, t \left[1 + \frac{1}{N} + \frac{(X_i - \bar{X})^2}{\Sigma(X_i - \bar{X})^2} \right]^{1/2}$$

The lower confidence limit about the regression line is given by:

$$(5) \qquad Y = Y_o + bX - S_{Y.X}\, t \left[1 + \frac{1}{N} + \frac{(X_i - \bar{X})^2}{\Sigma(X_i - \bar{X})^2} \right]^{1/2}$$

where:

$$S_{Y.X} = \left[\frac{\{Y_i - (\bar{Y} + b(X_i - \bar{X}))\}^2}{N - 2} \right]^{1/2}$$

Y_o = Calculated Y axis intercept;

t = Student's t for 2-tailed P = 0.10 and N-2 degrees of freedom;

$\bar{X}$ = The average of all target concentrations; and

$\bar{Y}$ = The average of all found concentrations.

The calculated reporting limit, X_d, is the value of X corresponding to a point on the lower confidence limit curve where the value of Y equals the value of Y on the upper confidence limit curve at X = 0. An example of the statistical analysis of reporting limit using the USATHAMA computer software is shown in Appendix C.

The calculated reporting limit will be reported as the CRL of the method, provided that at least one of the tested concentrations is at or below the calculated reporting limit. Otherwise, the lowest tested concentration is the minimum level that can be reported as the CRL. The CRL shall not be less than the lowest tested concentration. The CRL for Class 1 and Class 1B is reported to three significant figures. However, the CRL for Class 1A may only be reported to two significant figures.

The calculations described above must be performed on the entire certification performance data set in order to determine the method accuracy, as described in Section 4.8.3. If the calculated reporting limit for the complete data set (Class 1 and Class 1B only) is higher than required, points may be sequentially truncated, starting with the highest concentration. Truncation is not allowed for Class 1A certification. The calculations described above shall be performed using the truncated data set to obtain a new calculated reporting limit. This procedure may be repeated, sequentially

dropping the next highest concentration, until a satisfactory calculated reporting limit is obtained. The following limitations shall apply to the Class 1 and Class 1B truncation procedure:

- The data set must include the blank and the three lowest concentrations (0.5 TRL, 1 TRL, and 2 TRL); and
- After each truncation, the slope of the least square linear regression line shall not change by more than 10% from the slope for the total data set. If the slope changes by more than 10% after dropping a concentration, the calculated reporting limit may not be used as the CRL and further truncation is not acceptable.

The data provide an optimistic estimate of the method reporting limit because interferences found in natural samples will be absent. The highest tested concentration will represent the upper limit of reportable data. All sample measurements must be performed within the tested range. A calculated reporting limit higher than the highest target concentration indicates that either an invalid range was chosen or the method is not suitable for analysis of that compound.

The results for the total data set and each truncated set shall be provided in the Certification Performance Data Package.

These calculations are performed by the USATHAMA computer software. The CRL calculations cannot be performed for Class 2 methods. The TRL becomes the CRL for Class 2, which is only reported to two significant figures.

4.8.3 Accuracy

As calculated according to Section 4.8.2, the slope, b, of the least squares linear regression line of a plot of found versus target concentrations is a measure of the accuracy of the method. A slope (accuracy) of "plus one" (1.00) indicates 100% recovery over the complete analytical method and tested range. Failure to consider the intercept, if it is appreciably different from zero, could result in an erroneous estimate of the accuracy. Experimental values may deviate from this expected value. The certification data will provide an optimistic estimate of the method accuracy because interferences found in natural samples will be absent. The accuracy estimate for the complete certification data set is incorporated into the USATHAMA IRDMS (Section 6.6). The slope for the complete data set shall be used as the accuracy, even if the CRL was obtained from a truncated data set.

Estimates of accuracy cannot be calculated for Class 2 methods.

4.8.4 Standard Deviation

For Class 1, Class 1A, and Class 1B certification, the standard deviation, S, will be calculated at each target concentration according to:

$$(7) \qquad \text{Standard Deviation} = S = \left[\frac{\Sigma Y_i^2 - \frac{(\Sigma Y_i)^2}{N}}{N - 1} \right]^{1/2}$$

where:

Y_i = The found concentration; and

N = Total number of Y values at each target concentration.

This calculation is performed by the USATHAMA software.

4.8.5 Percent Inaccuracy

For Class 1, Class 1A, and Class 1B certification, the percent inaccuracy will be calculated at each target concentration according to:

$$(8) \qquad \text{Percent Inaccuracy} = \frac{\bar{Y} - X}{X} (100)$$

where:

X = Target concentration; and

$\bar{Y}$ = Average found concentration at the target concentration.

This calculation is performed by the USATHAMA software.

4.8.6 Percent Imprecision

For Class 1, Class 1A, and Class 1B certification, the percent imprecision will be calculated at each target concentration according to:

$$(9) \qquad \text{Percent Imprecision} = \frac{S}{\bar{Y}} (100)$$

where:

S = Standard deviation; and

$\bar{Y}$ = Average found concentration at the particular target concentration

This calculation is performed by the USATHAMA software.

4.9 Documentation

Upon completion of either precertification or certification performance testing, the Contractor Laboratory shall submit a Performance Data Package to the USATHAMA Analytical Branch for review. For precertification, the contractor shall submit the following Precertification Performance Data Package:

- Precertification method description in USATHAMA format containing laboratory-specific information concerning preparation and analysis of precertification calibration standards (Appendix B);
- Precertification calibration data, tabulation of concentration versus response (Appendix C);
- LOF and ZI test calculations and results for the precertification calibration curve (Appendices C and E);
- Certified calibration check standard(s) data (Class 1 and Class 1B only);
- Results of identification and purity analyses for all off-the-shelf reference materials (Section 6.5.3); and
- Checklist completed by the QAC (Appendix N).

For certification, the contractor shall submit the following Certification Performance Data Package:

- Final USATHAMA-approved copy of the Precertification Performance Data Package;
- Total method description in USATHAMA format containing approved deviations in the standardized method and laboratory-specific information concerning conduct of the method (Appendix B);
- Certification data, tabulation of found versus target concentration (Appendix C);
- LOF test calculations and results for the pooled data sets for found versus target concentrations (Appendices C and E);

- Linear regression, confidence bounds, reporting limit, accuracy, standard deviation, imprecision, and inaccuracy calculation results for the total data set and each sequential truncation, if performed (Appendix C);

- Narrative evaluation of effectiveness of the method for its intended use and shortfalls of the analytical method; and

- Checklist completed by the QAC (Appendix N).

In addition, the following should be included in the Certification Performance Data Package when applicable:

- Calibration data (initial and daily), tabulation of concentration versus response;

- Calibration curves (graphics with instrument response on the ordinate and concentration on the abscissa, not just the equation for the best fit calibration line) bracketing the tested range for each analyte (Section 6.4);

- Data and calculations demonstrating that the response for the Daily Calibration standard was within the required percentage (10% or 25%, depending on analysis type) of the response for the highest standard used during Precertification and Initial Calibration;

- For any chromatographic method, copies of the chromatograms from each day of certification analyses for the highest tested concentration and for the tested concentration closest to the CRL. Each chromatogram shall be labeled with the analysis date, analysis time, target concentration, test name, reference to the calibration curve used for quantification, and reference to the laboratory logbook where analytical activities were recorded. The identity of each peak shall also be labeled; and

- Spectra (e.g., IR, MS, NMR) for all target analytes.

APPENDIX C

Excerpts of Oak Ridge National Laboratory Comparison of USATHAMA and USEPA CLP QA Programs, Sections 5, 8, 10, 11

Section 5: QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability

Section 8: Calibration Procedures and Frequency

Section 10: Data Reduction, Validation, and Reporting

Section 11: Internal Quality Control Checks

5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability

Laboratory Certification

USATHAMA	EPA-CLP	COMMENTS
Contract award	Laboratory selection	USATHAMA specifies that the QA/QC plan must be documented and in practice before samples arrive. EPA-CLP requires a documented QA/QC SOP, but does not specify a timetable.
Development of Project QC Plan	Development of written QA/QC standard operating procedure (SOP) containing these essential elements:	
A statement of adherence or reference to the USATHAMA QA Program	Organization and Personnel QA policy and objectives QA organization Personnel training Document control and revisions	
A detailed account of how the QA Program will be implemented		
A description of the organization, responsibilities, and decision-making authorities of the contractor project team	Facilities and Equipment Procurement and inventory procedures Preventive maintenance	
A description of sampling team and analyst training in technical skills, standard QC, and essential elements of QA Program	Analytical Methodology Calibration and operating procedures	
Procedures for sampling, preservation, and shipment of samples	Sample Custody	
Sample inspection and lot sizing	Quality Control Quality control procedures Control checks and internal audits Reference material analysis Blank analysis Matrix spike and matrix spike duplicate analysis Internal audits	
Instrument calibration		
Logs (field, instrument, sample, QC)		
Analytical reference materials		
Procedures for verifying and documenting the quality of lab water		
Control charts	Data Handling Data handling, reporting, and record-keeping procedures Data validation	
Methods and criteria for determining when sampling or analytical systems are out of control, including holding times		
Actions to be taken to correct out-of-control situations, and how actions will be reported and documented		
A list of personnel responsible for data review and sequence of review prior to submittal		

5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability (cont.)

USATHAMA	EPA-CLP	COMMENTS
Generation and submission of pre-certification performance data package	Preparation for performance evaluation samples	EPA-CLP requires the analysis of "blind" evaluation samples for evaluation of laboratory performance. USATHAMA requires analysis of certification samples which are not blind.
Precertification method description (preparation and analysis of standards)		
Standardized method written to be laboratory-specific		
Development of method	Tuning and GC/MS mass calibration	Assumption is made that GC/MS tuning is described as part of the method.
Submit documentation for proposed method		
Analytical procedures testing		
Documentation of method in standard format		
Generation of performance data packages		
Review by USATHAMA Analytical Branch		
Assignment of method number after final approval		
Precertification calibration data		
Construction of calibration curve		
Prepare and analyze each standard in duplicate to bracket desired range for certification TRL = Target Reporting Limit (designated by USATHAMA)	Construction of Calibration Curves	
Class 1	Pesticides	
Blank, 0.5, 1, 2, 5, and 10 times the TRL plus expanded range	Established retention time windows Run evaluation standard mix at three concentrations Run standard mix of pesticides Run individual Aroclors	
Class 1A and Class 1B		

5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability (cont.)

USATHAMA	EPA-CLP	COMMENTS
Blank, 0.5, 2, and 10 times the TRL + range extension (10% for inorganic and 25% for all others)	GCMS: semivolatiles and volatiles require 5 point calibration curve with specified concentrations of 20, 50, 80, 120, and 160 ngs	
Tabulate and graph response vs. concentration Lack of fit (LOF) Zero intercept (ZI)	Tabulation of calibration data GCMS: Relative response factors Relative standard deviation Calibration factors GC: % RSD % Breakdown	
Certified calibration check standard - Class 1 and 1B only	Verification of performance checks GCMS: System performance check Calibration check	
Class 1 Two calibration check standards should be analyzed, one at the beginning and one at the end of the day - near high end of range	GC: Retention time shifts % Breakdown	
Class 1B One calibration check standard should be analyzed at the beginning of the day. New high end of range		
Results of identification and purity analyses for all off-the-shelf reference materials		
Checklist completed by the QAC		
Approval by USATHAMA of Pre-certification Performance Data Package and Project QA Plan		
Generation and submission of Certification Performance Data Package Final USATHAMA-approved copy of the Precertification Performance		

5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability (cont.)

USATHAMA	EPA-CLP	COMMENTS
Data Package		
Total method description in USATHAMA format containing approved deviations in the standardized method and laboratory-specific information concerning conduct of the method	Submission of Standard Operating Procedures	
Initial calibration MTR = minimum testing range TRL = target reporting limit * = times		Calibration procedure for semivolatiles and volatiles for EPA-CLP resembles USATHAMA Class 1 more than Class 1A which is reserved for all GC/MS methods. However, USATHAMA calibration for pesticides (assuming Class 1) is more stringent than EPA-CLP.
Class 1 MTR; blank, 0.5, 1, 2, 5, *10, and *10TRL 7 standards + 2 check standards MTR + 1 range extension; 10 standards + 2 check standards (20, 50, 100, 100) MTR + 2 range extensions; 13 standards + 2 check standards (20, 50, 100, 200, 500, 1000, 1000)		
Class 1A MTR; blank, 0.5, 2, 10 and 10 TL; 5 standards MTR + 1 range extension; (50, 200, 200); 7 standards MTR + 2 range extension; (50, 200, 500, 2000, 2000); 9 standards	GCMS: semivolatiles and volatiles require a 5 point initial calibration at specified concentrations	
Class 1B - same as 1A plus 1 check standard		
Class 2 - 6 standards, blank, and 1 triplicate TRL		
Daily calibration		Daily calibration for USATHAMA requires analysis of a high standard twice whereas EPA-CLP requires analysis of a lower range standard.
Class 1/Class 1A/Class 1B 2 standards for MTR - *10 and *10 TRL 2 standards for MTR + 1 range	GCMS: 50 total ngs, standard analyzed each 12 hours	

5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability (cont.)

USATHAMA	EPA-CLP	COMMENTS
extension - *100 and *100 TRL 2 standards for MTR and 2 range extensions - *1000 and *1000 TRL Class 2 4 standards (MTR) and blank and 1 TRL (duplicate)	Response must be within 25% for organics of mean response of 5 initial calibration standards	
Certification samples (prepared in standard matrix) Class 1/Class 1B MTR: 24 Blank, 0.5, 1, 2, 5, and 10 TRL (4 consecutive days) MTR + 1 range extension: 36 Blank, 0.5, 1, 2, 5, 10, 20, 50, 100 TRL (4 days) MTR + 2 range extentions: 48 Blank, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, 500, and 1000 TRL (4 days) Class 1A MTR: 8 Blank, 0.5, 2, and 10 TRL (duplicate) MTR + 1 range extensions: 12 Blank, 0.5, 2, 10, 50, and 200 TRL (duplicate) MTR + 2 range extensions: 16 Blank, 0.5, 2, 10, 50, 200, 500, and 2000 TRL (duplicate) Class 2 MTR: 8 Blank, 1 TRL (quadruplicate)	Performance Evaluation Samples prepared by EMSL/LV are sent to laboratory	With USATHAMA certification samples, the participating laboratory knows immediately whether problems exist in sample preparation and/or analysis. However, this same knowledge is available to EPA-CLP laboratories only if the results of the evaluation samples are returned promptly.
Statistical Analysis of the Data Tabulation of found vs. target concentration LOF and ZI test calculations and	Data Package Sample Traffic Report Sample Data Summary Package Case narrative	

5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability (cont.)

USATHAMA	EPA-CLP	COMMENTS
results for the pooled data set for found vs. target concentration	Target compound results-(Form I) Tentatively identified compounds-(Form I)	
Linear regression Confidence bounds Reporting limit Accuracy Standard deviation Percent Imprecision (% RSD) Percent Inaccuracy	Surrogate spike analysis results-(Form II) Matrix spike/matrix spike duplicate-(Form III) Blank data-(Form IV and Form I)	EPA-CLP surrogate spike is a measure of percent inaccuracy and matrix spike/matrix spike duplicate is a measure of percent imprecision.
Narrative evaluation of effectiveness of method Checklist completed by QAC	Sample Data Package Case narrative Traffic reports Volatiles data QC summary Surrogate spike results, Form II Matrix spike results, Form III Method blank summary, For GC/MS tuning standard, Form V Sample data TCL results, Form I Ion chromatograms Mass Spectra Library search spectra for TIC Quantitation of TIC Manual work sheets Standards data Initial calibratin data, Form VI Continuing calibration data, Form VII Internal standards summary, Form VIII Raw QC data BFB mass spectra Blank data, Form I Ion chromatograms Mass spectra Library search spectra for TIC Quantitation of TIC Manual work sheets Matrix spike results, Form I Matrix spike duplicate results, Form I Semivolatiles data QC summary	

5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability (cont.)

USATHAMA	EPA-CLP	COMMENTS
Calibration data, tabulation of concentration vs. response (a) Initial (b) Daily	Surrogate spike results, Form II Matrix spike results, Form III Method blank summary, Form IV	
Calibration curves (instrument response on ordinate vs. concentration on abscissa)	GC/MS tuning standard, Form V Sample data TCL results, Form I Ion chromatograms Mass spectra Library search spectra for TIC Quantitation of TIC Manual work sheets Standards data Initial calibration data, Form VI Continuing calibration data, Form VII Internal standards summary, VIII Raw QC data BFB mass spectra Blank data, Form I Ion chromatogram Mass spectra Library search spectra for TIC Quantitation of TIC Manual work sheets Matrix spike results, Form I Matrix spike duplicate results, Form I Pesticides/PCB data QC summary Surrogate spike results, Form II Matrix spike results, Form III Method blank summary, Form IV Sample data TCL results, Form I Gas chromatograms Confirmation gas chromatograms Manual work sheets GPC chromatograms GC/MS raw spectra Standards data Evaluation standards summary, Form VIII	
Data demonstrating that the response for Daily Calibration standards was within required percentage of highest standard		
Copies of chromatograms for high and low standards - certification samples analysis date and time target concentration test name reference to calibration curve reference to analytical logbook each peak labeled		
Spectra for all target analytes		

5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability (cont.)

USATHAMA	EPA-CLP	COMMENTS
	Standards summary, Form IX Identification, Form X Chromatograms Raw QC data Blank data, Form I Gas chromatograms Matrix spike results, Form I Gas chromatograms and printouts Matrix spike duplicate results, Form I Gas chromatograms and printouts	
	Data evaluated for accuracy by NPO (National Program Office) and audited by EMSL/LV personnel	
	Quality control data goes into EMSL/LV database for trend analyses, etc.	
	On-site laboratory evaluation	

8. Calibration Procedures and Frequency

USATHAMA	EPA-CLP	COMMENTS
Initial calibration		
Frequency (a) 1st day of certification analyses (b) Instrumental start-up (not daily) (c) Analyzing different analytes (d) Daily calibration fails If samples are analyzed on the same day as initial calibration, one standard at the highest concentration must be analyzed after analyses are completed	Frequency Prior to analysis of samples and if daily calibration fails	Frequency requirements are equivalent.
Concentration of standards Class 1 MTR; blank, 0.5, 1, 2, 5, *10, and *10 TRL, 7 standards + 2 check standards MTR + 1 range extension; 10 standards + 2 check standards (20, 50, 100, 100) MTR + 2 range extensions; 13 standards + 2 check standards (20, 50, 100, 200, 500, 1000, 1000) Class 1A MTR; blank, 0.5, 2, 10, & 10 TRL; 5 standards MTR + 1 range ext.; (50, 200, 200); 7 standards MTR + 2 range ext.; (50, 200, 500, 2000, 2000); 9 standards Class 1B - same as 1A plus 1 check standard Class 2 - 6 standards, blank, and 1 triplicate TRL	Concentration of standards GC/MS (≈ Class 1A) Volatiles 20, 50, 100, 150, and 200 µg/L The % RSD for each calibration check compound must be less than or equal to 30.0% The minimum acceptable average relative response factor is 0.300, 0.250 for bromoform Semivolatiles 20, 50, 80, 120, and 160 total nanograms The % RSD for each calibration check compound must be less than or equal to 30.0% The minimum acceptable average relative response factor is 0.05	Calibration procedure for semivolatiles and volatiles for EPA-CLP resembles USATHAMA Class 1 more than Class 1A which is reserved for all GC/MS methods. However, USATHAMA calibration for pesticides (assuming Class 1) is more stringent than EPA-CLP.
Certified check standards Class 1 - two stds - beginning & end of day Class 1B - one std - beginning of day - near high end of range If acceptability limits are exceeded, immediate reanalysis occurs, followed by a new initial calibration if necessary	GC (≈ Class 1) Pesticides Evaluation standard Mixture of aldrin, endrin, and 4,4.'-DDT at concentrations of 20%, 50%, and 100% full-scale Individual standard mixes and aroclors	Certified USATHAMA check standards made from the stock solution used during certification allow a continual check of laboratory performance.

8. Calibration Procedures and Frequency (cont.)

USATHAMA	EPA-CLP	COMMENTS
	The % RSD for evaluation standard mix compounds must be <10.0%. The % breakdown for endrin or 4,4'-DDT must not exceed 20.0%. The calibration factor for each individual standard must not exceed a 15.0% difference for a quantitation run nor exceed a 20.0% difference for a confirmation run.	
<u>Daily calibration</u> Class 1, 1A, 1B zero-intercept Highest concentration standard is analyzed at beginning and end of day Response must be within 10% for inorganic and 25% for others of the mean response for the same concentration as determined for precertification and certification for the 1st 7 calibrations After 7 calibrations, response must agree within 2 standard deviations	GC/MS (≃ Class 1A) Volatiles 50 µg/L standard is analyzed every 12 hours The % difference for each calibration check compound must be less than or equal to 25.0%. The minimum relative response factor for the system performance check compounds is 0.300 (0.250 for bromoform)	Daily calibration for USATHAMA requires analysis of the high standard twice whereas EPA-CLP requires analysis of the lower range standard. The quality of data should be equivalent.
Corrective action Reanalyze daily standard Initial calibration repeated		
Non-linear or non-zero intercept Analyze low, middle, and high calibration standards at beginning of day and low and high standards at the end of the day. (If quadratic, four standards) Responses must fall within 2 std. deviations of the mean response	Semivolatile 50 total ngs standard is analyzed every 12 hours The minimum relative response factor for the system performance check compounds is 0.050 The % difference for each calibration check compound must be less than or equal to 25.0%	
Class 2 One blank and one calibration standard at the CRL analyzed at beginning and end of sample analysis	Pesticides Analyze evaluation standard Mix B and individual standard Mix A or B alternately after every 5 samples The % difference in retention time for the dibutylchlorendate must not exceed	

8. Calibration Procedures and Frequency (cont.)

USATHAMA	EPA-CLP	COMMENTS
	0.3% for capillary or 2.0% for packed column The % breakdown for 4,4'-DDT or endrin must not exceed 20.0%	
Reference Materials		
Standard Analytical Reference materials traceable to NBS	EMSL/LV provides standard materials from its QA Materials Bank for performing initial instrument calibration and as reference standards	USATHAMA provides reference materials to prepare all standard solutions. EPA also makes available QC samples intended for periodic (quarterly) use as independent checks on each laboratory's own QC activities. No practical difference
Interim reference material (a) Central QA Lab (b) EPA (c) NBS		
Off-the-shelf material (a) Positive identification (b) Estimate of purity		

10. Data Reduction, Validation, and Reporting

USATHAMA	EPA-CLP	COMMENTS
Data reporting		Note difference in reporting of soil/sediment data. Either report is acceptable if the end user is aware of the difference.
CRL = certified reporting limit		
Data is not adjusted by any correction factors (such as accuracy, % moisture, and dilution factor), but is reported in the as-received condition	Soil/sediment data is adjusted to Dry Weight Basis	
Class 1, 1A, 1B All values less than CRL will be reported as <RL	Values less than quantitation limit are reported with J qualifier	
Number of Significant Figures to be used in Reporting Data		
Class 1 and 1B No dilution - 3 significant figures Dilution - 2 significant figures Noncertified analytes - retention time	GC/MS: Report data to 2 significant figures	
Class 1A No dilution - 2 significant figures After dilution - 1 significant figure Screening for noncertified - 1 significant figure	GC-Pesticides: Report data to 2 significant figures	
Class 2 CRL - 2 significant figures Reported as >, <, = CRL		
Deliverables	Deliverables	
Specific instructions for format, coding, and submission are provided in the IRDMS User's Guide	Inorganic (1) Weekly process reports (2) Sample traffic report (3) Sample data package Tabulated results Raw data Copies of logbook entries	
	Organic (1) Narrative report (2) Sample traffic report (3) Quality control summary (4) Sample data (5) Raw sample data (6) Standards package (7) QC data package	

11. Internal Quality Control Checks

USATHAMA	EPA-CLP	COMMENTS
Types		
Class 1 and Class 1B Method blank Spikes of control analytes in standard matrices Class 1A (GC/MS) Method blank/surrogate spikes Surrogates spikes in every field sample Class 2 Method blank Spikes of control analytes in standard matrices	Inorganics Preparation blank analysis Interference check sample analysis ICP serial dilution analysis Matrix spike analysis Duplicate sample analysis Furnace AA QC Analysis (Method of Standard Addition may be required under certain conditions) Laboratory quality control sample analysis Organics Method blank analysis Surrogate spike analysis Matrix spike/Matrix spike duplicate analysis	USATHAMA does not require matrix spiking (as EPA perceives) for organics. Matrix spikes could easily be added to USATHAMA plan. Frequency should be as in CLP. Matrix spikes are probably not necessary if surrogates are added to each sample, unless surrogate recovery is low.
Frequency per lot		
Class 1 One - standard matrix method blank Three standard matrix spikes 2, 10, & 10 CRL Class 1A One - standard matrix method blank spike (surrogate, 10 CRL) All field samples spiked with surrogate - 10 CRL Class 1B One - standard matrix method blank One - standard matrix spikes - 10 CRL Class 2 (a) One - standard matrix method blank (b) One standard matrix spike - 1 CRL	Inorganics Preparation blank - every 20 samples received or with each batch of samples digested whichever is more frequent Interference check sample - analyzed at beginning and end of each analysis run or a minimum of twice per 8 hour working shift ICP serial dilution - each group of samples of a similar matrix type and concentration for each case of samples or for each 20 samples received, whichever is more frequent Spiked sample and duplicate sample - at least one for each group of samples of a similar matrix and concentration for each case of samples or for each 20 samples received, whichever is more frequent	

11. Internal Quality Control Checks (cont.)

USATHAMA	EPA-CLP	COMMENTS
	Laboratory control sample - one for each group of 20 samples of a similar matrix or for each batch of samples digested whichever is more frequent	
	Organics	
	Method blank analysis	Method blank requirements are equivalent.
	Volatiles For the analysis of volatile TCL compounds, a method blank analysis must be performed once for each 12-hour time period during the analysis of samples from: o each case, OR o each 14 calendar day period during which samples in a case are received (said period beginning with the receipt of the first sample in that sample delivery group), OR o each 20 samples in a case that are of similar matrix (water or soil) or similar concentration (soil only), whichever is most frequent, on each GC/MS system used to analyze samples	
	Extractables For the analysis of extractable TCL compounds, a method blank analysis must be performed once: o each case, OR o each 14 calendar day period during which samples in a case are received (said period beginning with the receipt of the first sample in that sample delivery group), OR o each 20 samples in a case that are of similar matrix (water or soil) or similar concentration (soil only), OR	

11. Internal Quality Control Checks (cont.)

USATHAMA	EPA-CLP	COMMENTS
	o whenever samples are extracted by the same procedure (separatory funnel or continuous extraction), whichever is most frequent, on each GC/MS or GC system used to analyze samples	
	Surrogate spike analysis All blanks, field samples, matrix spikes, and matrix spike duplicates will be spiked with surrogate compounds	
	Matrix spike analysis A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, once: o each case of field samples received, OR o each 20 field samples in a case, OR o each group of samples of a similar concentration level (soils only), OR o each 14 calendar day period during which samples in a case were received (said period beginning with the receipt of the first sample in that sample delivery group), whichever is most frequent.	See earlier comments on matrix spiking.

11. Internal Quality Control Checks (cont.)

USATHAMA	EPA-CLP	COMMENTS
Preparation Assigned sample number during logging-in process Spiked samples (excluding water samples) must be allowed to stand for one hour before continuing the analysis		
Data Reporting Class 1 Minimum of 3 significant figures Method blank: can be corrected - reported by concentration Control charts Class 1A 2 significant figures Method blank: can be corrected - reported by concentration Control charts Class 1B Minimum of 3 significant figures Method blank: can be corrected - Reported by concentration Control charts Class 2 Minimum of 2 significant figures No control charts	Data Reporting Reporting of quality control samples handled just as samples are Soil/sediment results are corrected for percent moisture and reported on a dry weight basis No corrections are made for method blanks	Method blanks can be corrected in USATHAMA plan, but cannot be corrected in CLP. Blank correction is fine, but any time this is done the value should be documented. CLP should require control charts at least for surrogates and internal standards. In earlier IFB's, control charts were required for internal standards.